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Adrianite, $\text{Ca}_{12}(\text{Al}_4\text{Mg}_3\text{Si}_7)\text{O}_{32}\text{Cl}_6$, a new Cl-rich silicate mineral from the Allende meteorite: An alteration phase in a Ca-Al-rich inclusion

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Abstract

Adrianite (IMA 2014–028), $\text{Ca}_{12}(\text{Al}_4\text{Mg}_3\text{Si}_7)\text{O}_{32}\text{Cl}_6$, is a new Cl-rich silicate mineral and the Si,Mg analog of wadalite. It occurs with monticellite, grossular, wadalite, and hutchinsonite in altered areas along some veins between primary melilite, spinel, and Ti,Al-diopside in a Type B1 FUN (Fractionation and Unidentified Nuclear effects) Ca-Al-rich inclusion (CAI), *Egg-3*, from the Allende CV3 carbonaceous chondrite. The mean chemical composition of type adrianite by electron probe microanalysis is (wt%) CaO 41.5, SiO_2 27.5, Al_2O_3 12.4, MgO 7.3, Na_2O 0.41, Cl 13.0, O=Cl –2.94, total 99.2, giving rise to an empirical formula of $(\text{Ca}_{11.69}\text{Na}_{0.21})(\text{Al}_{3.85}\text{Mg}_{2.88}\text{Si}_{7.23})\text{O}_{32}\text{Cl}_{5.80}$. The end-member formula is $\text{Ca}_{12}(\text{Mg}_5\text{Si}_9)\text{O}_{32}\text{Cl}_6$. Adrianite has the $I\bar{4}3d$ wadalite structure with $a = 11.981 \text{ \AA}$, $V = 1719.8 \text{ \AA}^3$, and $Z = 2$, as revealed by electron backscatter diffraction. The calculated density using the measured composition is 3.03 g/cm^3 . Adrianite is a new secondary mineral in Allende, apparently formed by alkali-halogen metasomatic alteration of primary CAI minerals such as melilite, anorthite, perovskite, and Ti,Al-diopside on the CV chondrite parent asteroid. Formation of secondary Cl-rich minerals sodalite, adrianite, and wadalite during metasomatic alteration of the Allende CAIs suggests that the metasomatic fluids had Cl-rich compositions. The mineral name is in honor of Adrian J. Brearley, mineralogist at the University of New Mexico, U.S.A., in recognition of his many contributions to the understanding of secondary mineralization in chondritic meteorites.

Keywords

Adrianite; $\text{Ca}_{12}(\text{Al}_4\text{Mg}_3\text{Si}_7)\text{O}_{32}\text{Cl}_6$; new mineral; wadalite group; alteration mineral; Ca-Al-rich inclusion; Allende meteorite; carbonaceous chondrite

Introduction

During a nanomineralogy investigation of the Allende meteorite, a new Cl-rich silicate, $\text{Ca}_{12}(\text{Al}_4\text{Mg}_3\text{Si}_7)\text{O}_{32}\text{Cl}_6$ with the $I\bar{4}3d$ wadalite structure, named “adrianite,” was identified

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in Ca-Al-rich inclusion (CAI) *Egg-3* (Fig. 1). The Allende meteorite, which fell at Pueblito de Allende, Chihuahua, Mexico, on February 8, 1969, is a CV3 (Vigarano type) carbonaceous chondrite. Much work has been performed on *Egg-3* (e.g., Meeker et al. 1983), which is a coarse-grained igneous Type B1 Fractionation and Unidentified Nuclear effects (FUN) CAI from Allende (Wasserburg et al. 2012).

Electron probe microanalysis (EPMA), high-resolution scanning electron microscope (SEM), and electron backscatter diffraction (EBSD) were used to characterize composition and structure of adrianite. Synthetic $\text{Ca}_{12}(\text{Al}_4\text{Mg}_3\text{Si}_7)\text{O}_{32}\text{Cl}_6$, $\text{Ca}_{12}(\text{Al}_2\text{Mg}_4\text{Si}_8)\text{O}_{32}\text{Cl}_6$, or $\text{Ca}_{12}(\text{Mg}_5\text{Si}_9)\text{O}_{32}\text{Cl}_6$ has not been reported to date. We describe here the first occurrence of $\text{Ca}_{12}(\text{Al}_4\text{Mg}_3\text{Si}_7)\text{O}_{32}\text{Cl}_6$ in a meteorite, as a new alteration mineral in a CAI from a carbonaceous chondrite, and discuss its origin and significance for secondary alteration processes that affected CV chondrites (e.g., Brearley and Krot 2012). Preliminary results of this work are given by Ma and Krot (2014b).

Mineral name and type material

The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2014–028) (Ma and Krot 2014a). The mineral name is in honor of Adrian J. Brearley (b. 1958), mineralogist and cosmochemist at the University of New Mexico, in recognition of his many contributions to meteorite mineralogy. He is one of the leading authorities on alteration mineralogy studies of chondritic meteorites. The holotype specimen is in section MQM803 in G.J. Wasserburg's Meteorite Collection of Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, U.S.A. This section also hosts holotype hutchinsonite (IMA 2013–029; Ma and Krot 2014c).

Occurrence and associated minerals

Egg-3 is a coarse-grained igneous Type B1 CAI with a core composed of normally zoned melilite (Åk_{46-76}) and Ti,Al-diopside (in wt%: 1.9–11.5 TiO_2 , 17.2–21.7 Al_2O_3), nearly pure anorthite and MgAl-spinel, and a mantle composed of gehlenitic melilite (Åk_{14-34}) poikilitically enclosing rounded inclusions of Ti,Al-diopside (in wt%: 10.3–16.4 TiO_2 , 17.8–20.3 Al_2O_3) and spinel (Fig. 1). The coarser spinel grains form a nearly continuous layer in the middle of the melilite mantle. The CAI is surrounded by several rims (from inside outward) (1) a multilayered Wark-Lovering rim (Wark and Lovering 1976) made of melilite + perovskite, Ti,Al-diopside, and forsterite layers, (2) a forsterite-rich accretionary rim (Krot et al. 2001) composed of forsterite overgrown by secondary ferroan olivine, (3) a fine-grained matrix-like rim largely composed of ferroan olivine and nepheline, and (4) a discontinuous layer of salite-hedenbergite pyroxenes and andradite.

The CAI experienced ion-alkali-halogen metasomatic alteration that largely affected its primary melilite and resulted in the formation of diverse secondary minerals depending on the melilite composition (Brearley and Krot 2012). Gehlenite-rich melilite of the Wark-Lovering rim is almost completely replaced by sodalite, nepheline, and Na-bearing (up to 1 wt% Na_2O) plagioclase; grossular is minor (Figs. 2a and 2b). Spinel in the Wark-Lovering

rim is enriched in FeO (up to 10 wt%). Gehlenite-rich melilite in the mantle is crosscut by grossular and Na-bearing plagioclase veins (Figs. 2b and 2c). The plagioclase/grossular ratio in veins decreases toward the CAI core. Åkermanite-rich melilite in the core is largely replaced by grossular, monticellite, Ti-free Al-diopside, and wollastonite; secondary forsterite, kushiroite, wadalite, hutcheonite, and adrianite are minor (Figs. 2d and 2e). The core anorthite experienced relatively minor alteration; it is crosscut by veins of grossular, Na-rich melilite (up to 4.7 wt% Na₂O), kushiroite, and celsian (BaAl₂Si₂O₈) (Figs. 2e and 2f). A trace amount of Ni-Fe-rich metal is present in the CAI core.

Adrianite occurs in contact with monticellite and grossular, plus nearby wadalite and hutcheonite in alteration areas along some cracks between primary melilite, spinel, and Ti,Al-diopside in the core area of the CAI (Figs. 3–5). Hutcheonite [Ca₃Ti₂(SiAl₂)O₁₂] is a newly found garnet mineral (Ma and Krot 2014c).

X-ray elemental mapping reveals a zoned distribution of Na- and/or Cl-rich secondary minerals: nepheline and sodalite occur largely in the peripheral part of the CAI, whereas wadalite and adrianite are found exclusive in its core; the melilite mantle virtually lack Na- and Cl-rich secondary minerals (Fig. 1).

Appearance, physical and optical properties

Adrianite occurs as small, irregular, single crystals, 2–6 µm in size (Figs. 3–5), which are the holotype material. Color, luster, streak, hardness, tenacity, cleavage, fracture, density, and optical properties could not be determined because of the small grain size. Adrianite is non-cathodoluminescent under the electron beam in an SEM. The calculated density is 3.03 g/cm³ using the empirical formula.

Chemical composition

Backscattered electron (BSE) images were obtained using a ZEISS 1550VP field emission SEM and a JEOL 8200 electron microprobe with AsB (angle selective backscatter) and solid-state BSE detectors, respectively. Quantitative elemental microanalyses were carried out using the JEOL 8200 electron microprobe operated at 10 kV (for smaller interaction volume) and 5 nA in focused beam mode. Analyses were processed with the CITZAF correction procedure (Armstrong 1995) using the Probe for EPMA program from Probe Software, Inc. Analytical results are given in Table 1. No other elements with atomic number greater than 4 were detected by WDS scans. The empirical formula (based on 32 oxygen atoms pfu) of type adrianite is (Ca_{11.69}Na_{0.21})(Al_{3.85}Mg_{2.88}Si_{7.23})O₃₂Cl_{5.80}. This Cl-rich silicate is a new wadalite group mineral with Si⁴⁺ > Al³⁺ at tetrahedral sites in the structure. The general formula is Ca₁₂(Si,Al,Mg)₁₄O₃₂Cl₆. The ideal formula of the holotype material is Ca₁₂(Al₄Mg₃Si₇)O₃₂Cl₆. The end-member formula is likely Ca₁₂(Mg₅Si₉)O₃₂Cl₆, which requires SiO₂ 34.23, MgO 12.76, CaO 42.59, Cl 13.46, O=Cl –3.04, total 100.0 wt%. Associated wadalite has an empirical formula of (Ca_{11.58}Na_{0.09})(Al_{7.42}Mg_{1.29}Si_{5.39})O₃₂Cl_{5.66}. Nearby primary melilite has an empirical formula of Ca_{2.00}(Mg_{0.51}Al_{0.45})(Si_{1.55}Al_{0.45})O₇, and Ti,Al-diopside shows an empirical formula of Ca_{1.00}(Mg_{0.52}Al_{0.25}Ti_{0.18})(Si_{1.45}Al_{0.55})O₆ with ~18 wt% Al₂O₃ and ~7 wt% TiO₂.

Crystallography

Single-crystal electron backscatter diffraction (EBSD) analyses at a sub-micrometer scale were performed using an HKL EBSD system on the ZEISS 1550VP SEM, operated at 20 kV and 6 nA in focused beam mode with a 70° tilted stage and in a variable pressure mode (25 Pa) (Ma and Rossman 2008, 2009). The EBSD system was calibrated using a single-crystal silicon standard. The structure was determined and cell constants were obtained by matching the experimental EBSD patterns with structures of wadalite, grossular, and mayenite.

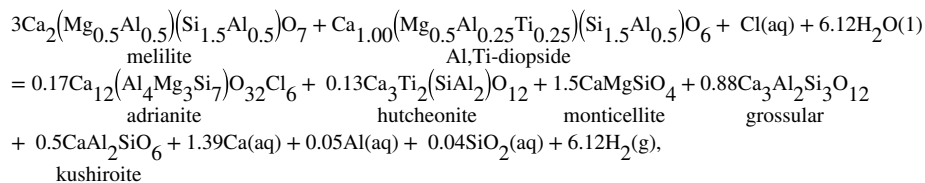
The EBSD patterns can be indexed nicely by the $\bar{1}\bar{4}3d$ wadalite structure and give a best fit using the wadalite structure from Feng et al. (1988) (Fig. 6), with a mean angular deviation of 0.31°, showing $a = 11.981 \text{ \AA}$, $V = 1719.8 \text{ \AA}^3$, and $Z = 2$.

The X-ray powder-diffraction data (in angstroms for $\text{CuK}\alpha_1$, Bragg-Brentano geometry) are calculated from the cell parameters and the atomic coordinates of Feng et al. (1988) with the empirical formula from this study, using PowderCell version 2.4. The strongest calculated lines are [d in angstroms, intensity, (I), scaled to 100 for the most intense peak, (hkl)] [2.679, 100, (420)], [2.446, 36, (422)], [2.995, 32, (400)], [1.661, 28, (640)], [1.601, 28, (642)], [4.891, 14, (211)], [2.187, 14, (521)], and [1.729, 14, (444)].

Origin, significance, and implications

Adrianite, $\text{Ca}_{12}(\text{Al}_4\text{Mg}_3\text{Si}_7)\text{O}_{32}\text{Cl}_6$, is the Si,Mg analog of wadalite $\text{Ca}_{12}(\text{Al}_{10}\text{Si}_4)\text{O}_{32}\text{Cl}_6$. It is a new member of the wadalite group in the mayenite supergroup. Its end-member may be $\text{Ca}_{12}(\text{Mg}_5\text{Si}_9)\text{O}_{32}\text{Cl}_6$.

Adrianite is found only in altered regions of the Allende CAI, in close association with secondary monticellite, grossular, hutchonite, and wadalite (Figs. 3–5). Mineralogical observations, thermodynamic analysis, and oxygen and ^{26}Al - ^{26}Mg isotope systematics of grossular, monticellite, and wollastonite in CV chondrites indicate that these minerals resulted from in-situ alteration of the Allende CAIs during fluid-assisted thermal metamorphism of the CV chondrite parent asteroid below 600 °C, ~3–4 Myr after CAI formation (Krot et al. 2007; Brearley and Krot 2012). Based on these observations, we infer that adrianite is also a secondary alteration product, formed by iron-alkali-halogen metasomatic alteration of the primary melilite, perovskite, and Ti,Al-diopside in the CAI on the Allende parent asteroid. *Egg-3* experienced open-system, post-crystallization alteration that resulted in the addition of Si, Na, Cl, and Fe, and loss of Ca (Fig. 1); Al, Ti, and Mg were also mobile during the alteration. One possible reaction to account for adrianite formation in *Egg-3*, based on simplified or end-member formulas, may be expressed as:



where grossular, monticellite, and kushiroite (CaTs, Ti-free Al-rich pyroxene) are among the common secondary minerals, and melilite and Al,Ti-diopside are the major primary minerals that were altered.

Secondary Cl-rich minerals identified in CAIs now include sodalite, chlormayenite (previously known as “brearleyite”; Ma et al. 2011), wadalite, and adrianite. Each and every new mineral identified in meteorites provides new information on forming conditions. Adrianite is one of six new secondary minerals discovered in Allende CAIs, helping to reveal alteration processes on the parent body.

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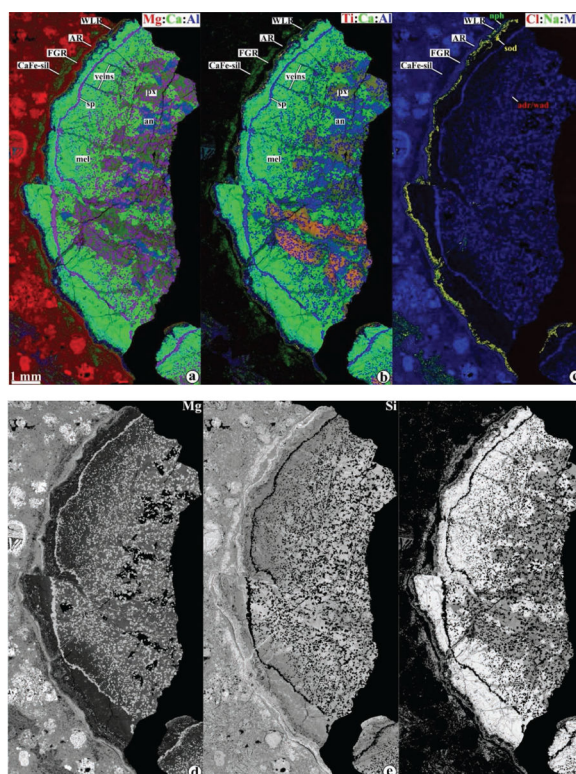


Figure 1.

Combined X-ray elemental maps in (a) Mg (red), Ca (green), and Al (blue); (b) Ti (red), Ca (green), and Al (blue); (c) Cl (red), Na (green), and Mg (blue); and X-ray elemental maps in (d) Mg, (e) Si, and (f) Ca of the Allende Type B1 CAI *Egg-3*. The CAI experienced open-system alteration that resulted in the addition of Si, Na, Cl, and Fe, and loss of Ca. adr = adrianite; an = anorthite; AR = forsterite-rich accretionary rim; CaFe-sil = layer of salite-hedenbergite pyroxenes and andradite; FGR = fine-grained matrix-like rim; mel = melilite; nph = nepheline; px = Ti,Al-diopside; sod = sodalite; sp = spinel; wad = wadalite; WLR = Wark-Lovering rim. Sodalite is yellow in c, derived from a combination of Cl (red) and Na (green). (Color online.)

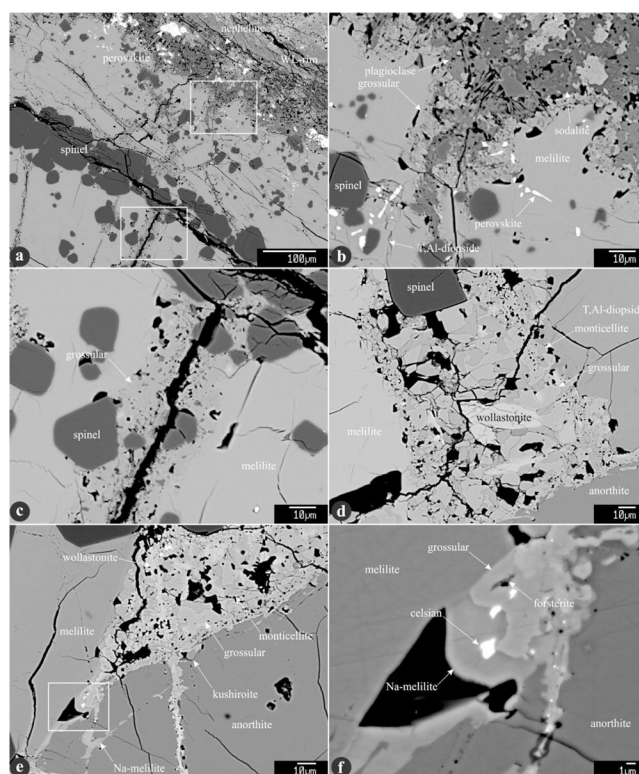


Figure 2.

SEM BSE images showing secondary mineralization in different parts of *Egg-3*. Regions outlined in **a** and **e** are shown in detail in **b** and **c** and **f**, respectively. (**a–c**) Gehlenitic melilite near the Wark-Lovering (WL) rim is replaced by nepheline, sodalite, and Na-bearing plagioclase. Gehlenitic melilite in the mantle is crosscut by plagioclase-grossular veins. The abundance of anorthite in veins decreases toward the CAI core. (**d–f**) In the CAI core, åkermanitic melilite is replaced by grossular, monticellite, wollastonite, and Ti-free Al-diopside. Anorthite is crosscut by veins of grossular, Na-melilite, forsterite, kushiroite, and celsian.

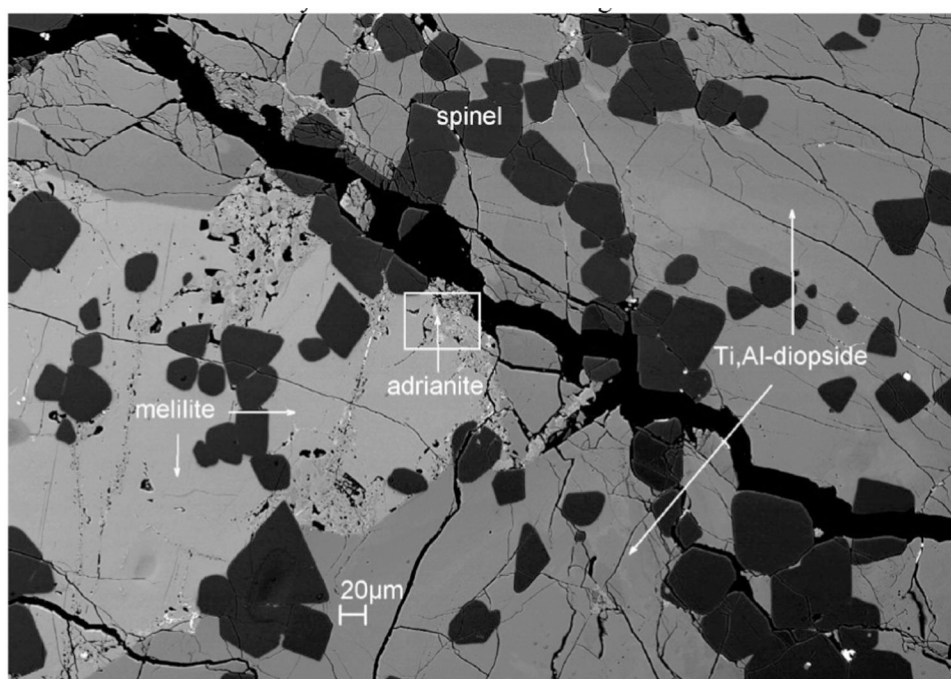


Figure 3. SEM BSE image showing part of the Type B1 CAI *Egg-3* in MQM803. The location of adrianite is indicated by the box and shown in Figure 4.

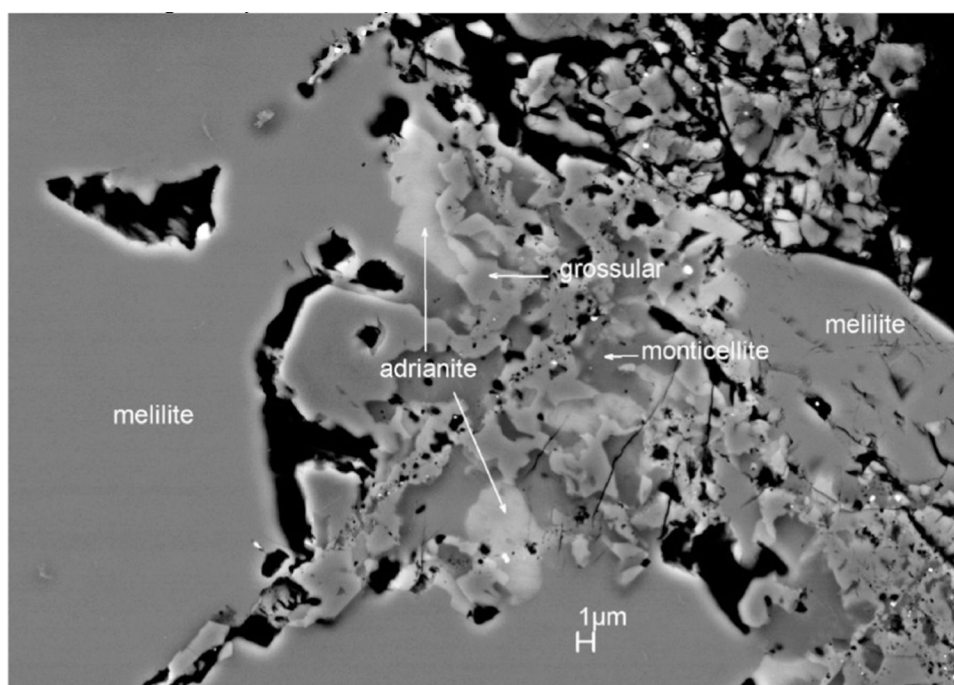


Figure 4. Enlarged BSE image revealing adrianite with grossular and monticellite in the altered area between primary melilite crystals.

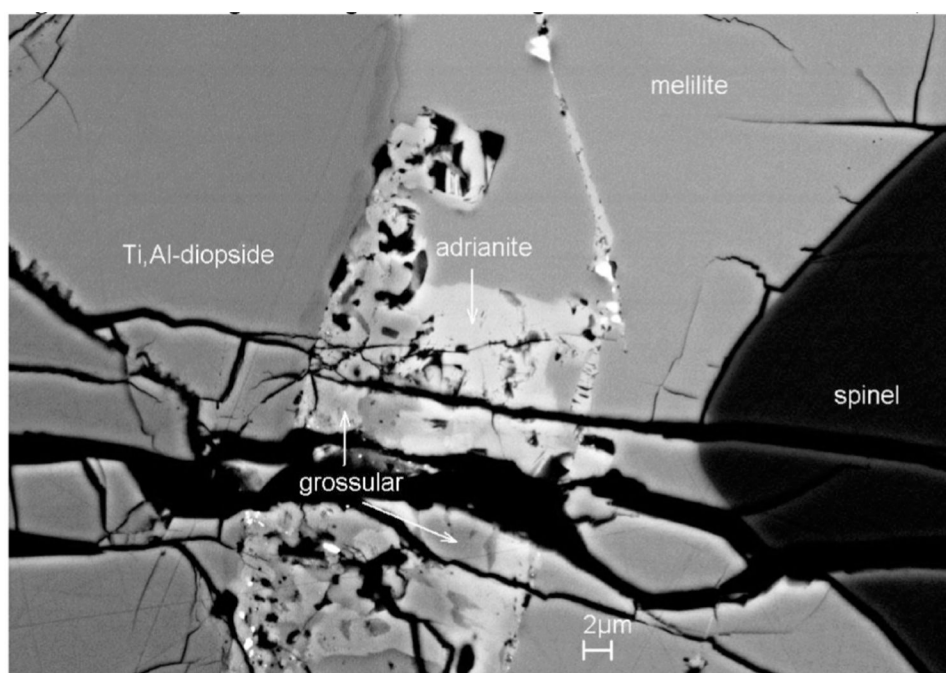


Figure 5.
BSE image showing adrianite with grossular between melilite and Ti,Al-diopside.

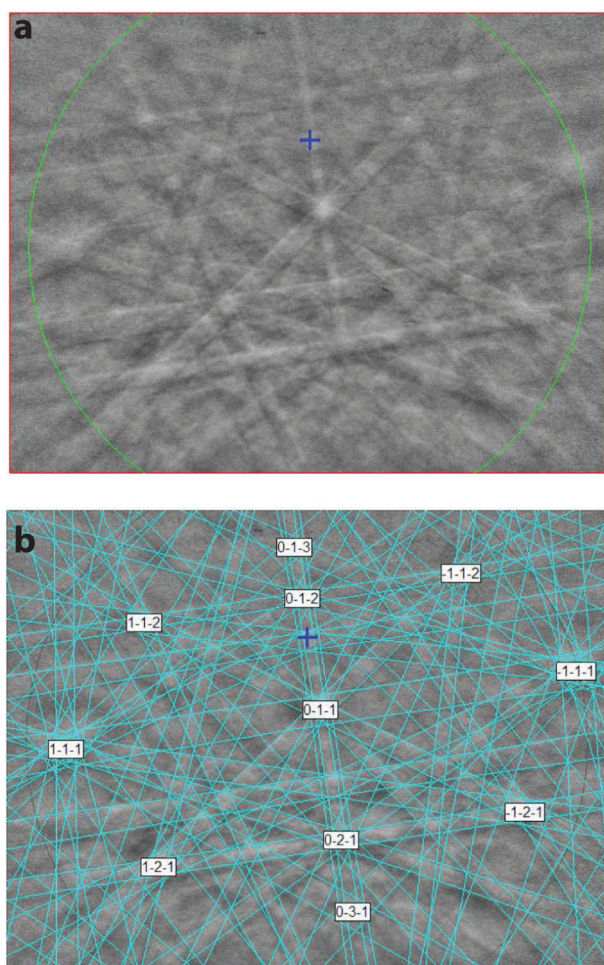


Figure 6. (a) EBSD pattern of the adrianite crystal in Figure 2, and (b) the pattern indexed with the $I\bar{4}3d$ wadalite structure. (Color online.)

Table 1.EPMA data for type adrianite and nearby wadalite in *Egg-3*

Constituent (wt%) ^a	Adrianite n = 3 ^b	Wadalite n = 3	Probe standard
SiO ₂	27.5(3) ^c	20.6(1)	grossular
Al ₂ O ₃	12.4(2)	24.0(5)	grossular
MgO	7.3(2)	3.3(4)	forsterite
CaO	41.5(4)	41.2(2)	grossular
Na ₂ O	0.41(3)	0.2(1)	albite
Cl	13.0(3)	12.73(3)	sodalite
–O	2.94(7)	2.87(1)	
Total	99.2	99.2	

^aDetection limit at 99% confidence: 0.07 wt% Si, 0.07 wt% Al, 0.03 wt% Mg, 0.04 wt% Ca, 0.05 wt% Na, 0.04 wt% Cl.^bNumber of point analyses.^cStandard deviation in parentheses.